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Tailoring Dynamic Mechano-Responsive Polymer Systems for
Energy Dissipation and Damage Resistance

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Final Report

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14. ABSTRACT Over the course of this grant, our group worked on ionomer (ethylene-co-methacrylic acid or EMAA) and metal ion (primarily Cu ²⁺ and Ag ⁺) containing polyelectrolyte assemblies. We are interested in how the strength of complexation between polymers and crosslink density can influence properties, including mechanical properties. Using electrostatic directed self-assembly, or the layer-by-layer technique, allows for the modulation of secondary interactions within these thin films and coatings. This in term can result in the variation of a range of mechanical properties, including toughness, modulus, hardness, and the ability to self-heal. We have found that ionomer assemblies can be made into free-standing thin films, and that the toughness of these materials is dependent on both the assembly conditions and post-assembly annealing. Additionally, we have shown that for copper ion containing films, the ions act as crosslinking agents increasing hardness and modulus. On the other hand, incorporation of Ag ions increases the ability of these thin films to self-heal.					
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Over the course of this project, our group worked on ionomer (ethylene-co-methacrylic acid or EMAA) and metal ion (primarily Cu^{2+} and Ag^+) containing polyelectrolyte assemblies. We are interested in how the strength of complexation between polymers and crosslink density can influence properties, including mechanical properties.

Polyelectrolytes are water soluble polymers that carry a charge on the monomer repeat unit. Ionomers are a related class of polymer, with only some portion of the repeat groups being charged. Oppositely charged polyelectrolytes (or ionomers) will strongly associate with one another, in a process called complexation. This process is entropically driven, as the complex formation frees both the solvation shell around the polymer chains as well as the small molecule counter ions associated with the charge groups. In addition to bulk complex formation, this process can also be directed onto surfaces via a method known as the layer-by-layer (lbl) process, in which a substrate is exposed sequentially to oppositely charged solutions until a sufficient number of layers are adsorbed onto the substrate.

Experimental/Instrumentation



Figure 1: Slide stainer for film assembly.

Films/coatings are assembled from commercially available materials, either from Sigma Aldrich, VWR, or Dupont (EMAA ionomers).

Polyelectrolyte multilayers are assembled using a biological slide stainer, fig. 1, controlled by a computer interface, which is a robotic arm that moves the substrates to be used from one polyelectrolyte solution to a rinse bath, to the other polyelectrolyte solution. Complexes are formed simply by mixing solutions of oppositely charged polyelectrolytes/ionomers. For ion containing films, metal ions are complexed to polyethylene imine in solution and then this complex is used in film assembly. Although polyelectrolytes are generally water soluble, EMAA is not, and was deposited out of either THF or THF/water. Characterization of these materials was done using techniques including stylus profilometry, contact angle

measurements, FTIR, nanoidentation, zeta potential measurements, light scattering, TEM, SEM, DMA, TGA, and AFM. More detailed descriptions of these processes can be found in the literature.^{1,2}

Technical Results:

1. Ionomer-Polyelectrolyte Materials

Ethylene-co-methacrylic acid ionomers were obtained from Dupont (sold under the commercial name surlyn). Coatings and complexes of this material and linear polyethylene imine (LPEI, a secondary amine containing polyelectrolyte) were fabricated by previously described methods.¹ Metal ions were incorporated into these assemblies by soaking the films in various salt solutions. Previously published solutions¹ show that complexation with LPEI results in changes in DSC data corresponding to a decrease in ethylene crystallinity and the incorporation of new electrostatic interactions within the film. We have also developed a method to produce freestanding films from these materials, which involves soaking the materials in basic solution which deprotonates the amine groups, lessening the interaction between the film and the glass substrate. Annealing the film as well improves optical properties. Tensile testing of

these materials shows that annealing also improves mechanical properties. Figure 2 shows the (a) results of tensile testing of 5 micron thick freestanding films (b) that have been processed in different ways. The weakest film (lowest toughness, taken as the area under the stress-strain curve, lowest strain

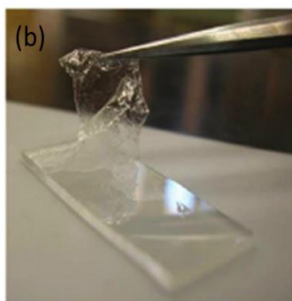
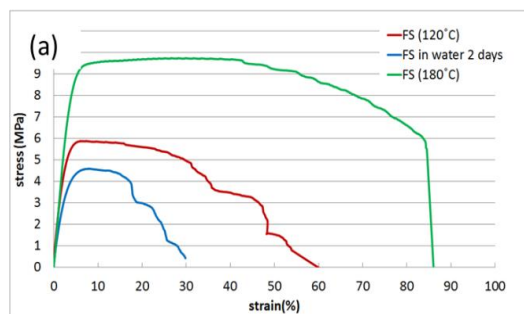


Figure 2: (a) tensile testing data for free standing EMAA-polyethylene imine assemblies processed under various conditions, and (b) an image of an EMAA-polyethylene imine assembly being removed from a glass substrate in order to create free standing assemblies.

and lowest stress to failure) has only been soaked in basic aqueous solution. The next stronger film has been annealed at 120°C, and the strongest film has been annealed at 180°C. The EMAA deposits as aggregated colloidal particles and annealing will allow for chains to diffuse and increase connectivity in the film. These tensile testing

results demonstrate our ability to improve mechanical properties of EMAA materials with different types of processing.

EMAA is generally a hydrophobic material due to the majority ethylene component. EMAA is also the majority component in our assemblies, as these form as roughly charged matched materials (i.e. equivalent numbers of positive and negative charges) and the methacrylic acid groups are only ~5 mol% of the copolymer. AFM images (as well as profilometry analysis) show that the film surfaces are very rough. This is because the EMAA is more of a dispersion of colloidal particles in THF rather than a true

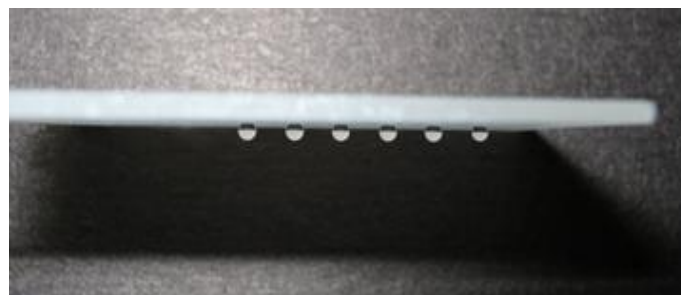


Figure 3: Water droplets adhering to the surface of an EMAA/LPEI film after inversion. This is due to both the chemical nature of the surface but also the rough structure of the film.

dispersion, and deposits onto the substrate as a collection of particles. This results in a surface that has very good adhesion properties of water droplets, similar to flower petals. Figure 3 shows water droplets adhering to a film surface after being inverted. Similar structures are being investigated for possible use as water collecting surfaces.

2. Metal Ion Containing Films

In addition to looking at ionomer containing materials, we have been pursuing the incorporation of metal ions into polyelectrolyte assemblies. Metal-ligand coordination bonds have different strengths than the other electrostatic interactions between oppositely charged polymers, adding a range of secondary interactions within the polyelectrolyte multilayer. Although films were assembled with a range of ions (shown in figure 4), we chose a bivalent (Cu^{2+}) and a monovalent (Ag^+) ion to be more extensively studied. These metal ions are first complexed in solution with branched PEI, a polyelectrolyte containing primary, secondary, and tertiary amine groups, in ratios such that there is an

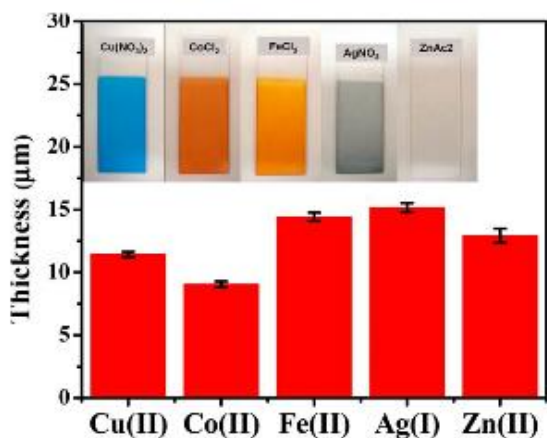


Figure 4: Film thicknesses and optical images of various films assembled with different metal ions, from reference 2.

to find both Young's modulus and hardness. From this we can infer that although the copper ions are complexed with the BPEI prior to film assembly, they are still able to interact with the polyanion chains,

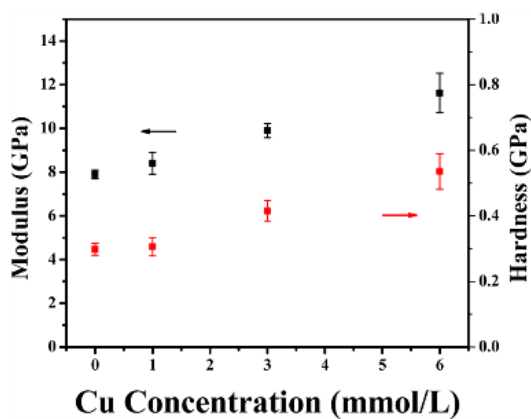


Figure 5: Both modulus and hardness of lbl assemblies increase with increasing amounts of incorporated Cu(II) ions.²

silver ions was shown to be fluorescent, and this was also true for the films we assembled. This might lead to the development of sensing materials. These films were observed to not be as mechanically strong as the copper containing films, which leads us to believe that the divalency of the copper ions is what permits the interaction with the polyanion in the assemblies. However, the Ag ion containing films were observed to have the ability to self-heal large (mm scale) scratches in the presence of water.

excess of amine groups. This complex is then used to assemble lbl films in a similar manner as uncomplexed polyelectrolyte.

a) Cu containing films

Copper(II) ion containing films were assembled and these results are published.² Significant results from this work include that it is possible to displace the various Cu(II)-ligand bonds within the lbl assemblies with molecules that bind more strongly to the copper such as EDTA, meaning that these bonds are dynamic in nature. Also significant was the observation that including the copper ions increases the mechanical strength of the films (figure 5), measured by nanoindentation acting as a type of crosslinker. This may be through electrostatic interactions or other types of metal-ligand interactions.

b) Ag ion containing films

Films containing Ag⁺ ions, Ag nanoclusters (~5nm) and Ag nanoparticles (~100 nm) were fabricated in a method similar to the copper containing films (i.e. complexation between metal ions and amine containing polymer, then the assembly of that complex into thin films). This types of assemblies have often been shown to have anti-microbial properties in the literature. We, however, were interested in different properties including mechanical and optical. The complex of BPEI and

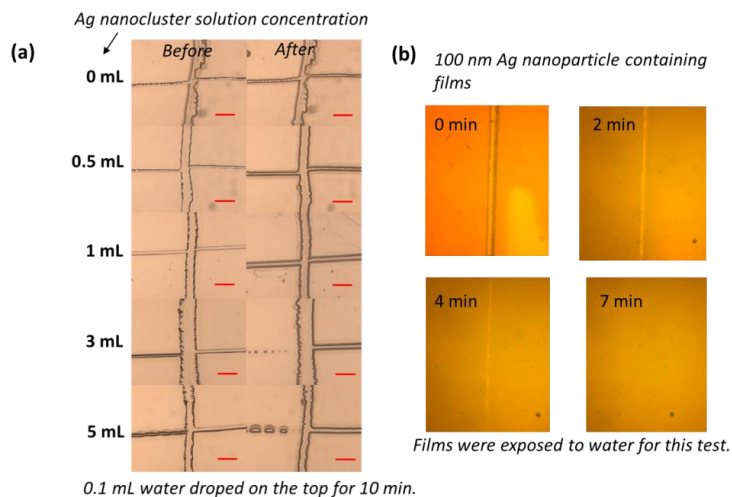


Figure 6: (a) Various Ag-NC (5 nm clusters of silver) containing films before and after being scratched and then exposed to water for 10 min. Increasing the concentration of Ag nanoclusters improves the material's ability to self-heal. (b) Ag nanoparticle (~100 nm in size) containing films under similar conditions. They are able to self-heal a similar scratch much more quickly than nanocluster containing films.

Three types of Ag containing assemblies were fabricated; Ag⁺ ion containing films, Ag⁺ ion nanocluster containing films (these nanoclusters have been measured by TEM to have an average size of 5 nm), and Ag nanoparticle containing films (these nanoparticles have been shown by TEM to have an average size of 100 nm). These three types of films, as well as

films containing no silver but only polyelectrolyte as a control, were scratched with a razor blade. The scratches were 2 – 3 mm wide made in films that were approximately 1 micron thick. Several drops of water were placed on the film (so the presence of humidity is required to activate this self-healing process) and within minutes some degree of self-healing is observed for both Ag-nanocluster containing and Ag-nanoparticle containing films. This can be seen in figure 6; part (a) shows that increase the concentration of Ag nanoclusters in the assemblies increases the amount of healing of a cross scratched into the film over a 10 minute period of time. Part (b) shows the same place on a scratch in a Ag-nanoparticle containing film over the course of 7 minutes. The scratch is no longer visible at the end of the 7 minute time period. Polyelectrolyte only and Ag⁺ ion containing films did not show any healing ability over the course of several hours. We have also observed that the incorporation of Ag⁺ ions decreases the water contact angle of these films. Although these results are still preliminary, we hypothesize that the inclusion of silver increases the ability of the films to swell with water, improving the ability to heal in the presence of water. However, a more thorough examination of both mechanical and rheological properties of these films is necessary to fully explain these observations.

Student/Workforce Training:

This grant has supported Ms. Hsiu-ching Huang and Ms. Xiayun Huang for a portion of their PhDs. They are both anticipated to graduate in August of 2014 with PhDs in mechanical engineering. This award also supported Mr. Ryan Davis for a portion of his degree (M.S. in materials science awarded in May 2013). Mr. Davis is currently working at Sandia National Labs.

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